

Final Report

Atomic Emission, Absorption and Fluorescence in the Laser-induced Plasma

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PI: James D. Winefordner

Department of Chemistry

University of Florida

Gainesville, Florida 32611

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During the reported time, a total of **12** manuscripts have been published or submitted for publication, **8** presentations have been made at domestic and international conferences, **1** patent have been registered.

I. First year: 2005-2006

The following problems have been set and solved.

1. Theoretical: further development of the radiative model of LIP. In particular, the two-temperature model of LIP and the model of LIP with strong initial asymmetry have been developed during the reported period. Plasma diagnostics was a part of this work and provided the model with necessary experimental inputs.
2. Practical: the theoretical model of LIP was used to calculate the composition of materials based on spectral data, with no standards to use. Also, the model was used to predict theoretically a type of a light detector that suits the best for analytical applications of laser induced breakdown spectrometry (LIBS).

Two-Temperature model

There is strong evidence that the LIP deviates from LTE conditions. To account for non-equilibrium conditions, a two-temperature model is developed. The model suggests different temperatures for electrons and heavy particles. The electron temperature deviates from that of heavy particles because of the slow rate of energy transfer between electrons and heavy particles caused by their large mass difference. The two temperatures are incorporated into the model by using fluid dynamic equations supplemented by the two equations of state: one for electrons and one for heavy particles. The ionization non-equilibrium is accounted for by incorporating ionization/recombination kinetics into the model.

Model of plasma with strong initial asymmetry

We have also developed and verified experimentally a theoretical model for an asymmetric expansion of laser induced plasmas into vacuum. It was proven that the self-similar plasma

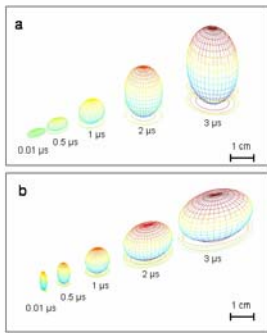


Figure 1. Calculated plasma shapes.

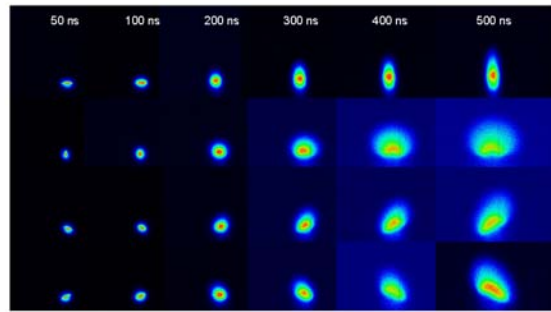


Figure 2. Experimentally observed evolution of plasma shape.

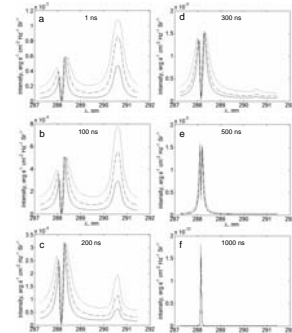


Figure 3. Spectra calculated along plasma ellipsoidal axes

expansion with a velocity proportional to the distance from the center does not hold true for thermally anisotropic plasmas with radiative losses. The model predicted the flip over effect (Fig.1) observed experimentally (Fig.2). The spectra were calculated for silicon plasma expanding asymmetrically into vacuum. It was shown (Fig.3) that spectral line intensities are

strongly dependent upon the direction of spectrum observation. This result is important for both the spectrochemical plasma analysis and plasma diagnostics based on plasma symmetry.

Standardless spectral analysis using radiative model of LIP with Monte Carlo optimization

Our radiative model of LIP allows a back-calculation of the composition of the plasma. The model uses experimentally obtainable data: LIP spectra, initial plasma size and initial plasma temperature. We have demonstrated that the model works satisfactory for plasmas expanding

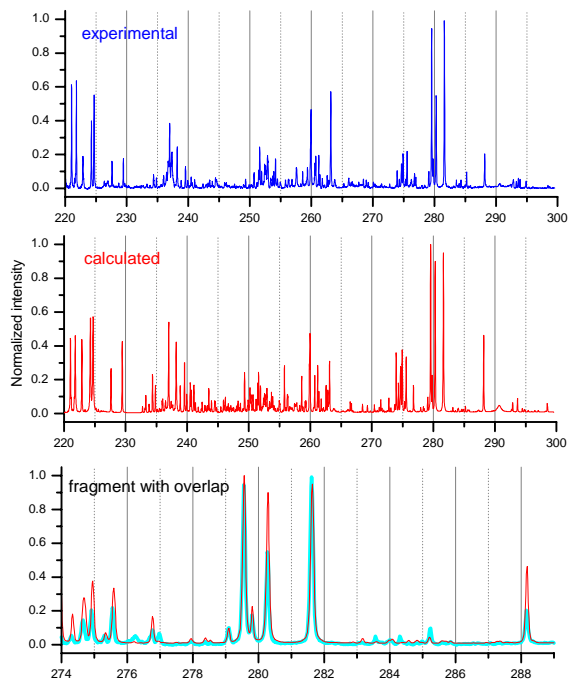


Figure 4. a) Experimental spectrum from Al alloy; b) Synthetic spectrum for the initial temperature of 22000 K; c) Narrow band overlap of the experimental and synthetic spectra.

into vacuum. Calculations and measurements are performed on a binary SiC system, on a series of multi-component aluminum samples doped with Si, Mg, Cu, Zn, Fe, and on pure iron, silicon and carbon. Monte Carlo optimization is used for finding initial plasma temperature and number densities. Good agreement (Fig.4) is obtained between the computed and the experimental spectra. We are able, therefore, roughly predict the plasma composition and plasma temperature using easily measurable initial plasma size and plasma spectrum. This can be considered as absolute analysis of the gaseous components of the plasma. If stoichiometric ablation is assumed, the method can also estimate the elemental composition of the condensed phase material.

A similar model is under development for LIP expanding into an ambient gas as this is the most practical analytical situation. This modified model describes the expansion of a LIP accompanied by a shock wave into an argon atmosphere. Our results clearly demonstrate that on the basis of the model, the inverse problem, e.g., the determination of intrinsic plasma

characteristics from the experimentally determined parameters, can be solved.

Comparison of light detectors for LIBS based on experiment and model calculations

We performed a series of simulations to answer the question: which detector is more suitable for application in LIBS. Answering the question is important both for the analytical groups and instrumental companies as it affects the analysis quality and instruments pricing. We demonstrated that when time-resolved measurements are not demanded, the charge-coupled device (CCD) is an adequate choice for LIBS. In many cases, the CCD performs better than the intensified charge-coupled device (ICCD) while its cost is significantly lower. We compare the results of our computer simulations to the results obtained experimentally using a LIBS echelle spectrometer equipped with either a CCD or ICCD. A dominant source of noise for both

detectors is the photon noise which is determined by the Poisson statistics. Other noises (i.e. the

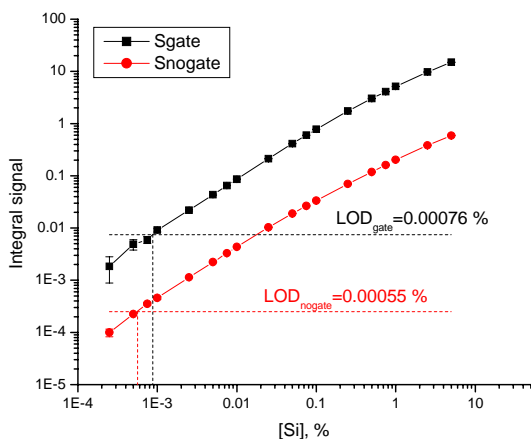


Figure 5. Theoretical calibration plots for Si in Al. The use of a non-gated detector (CCD) yield slightly better detection limits compared to a gated detector (ICCD)

read-out noise, dark current noise, etc.) are negligible due to very short exposure times (μs -ms) and high quality of the detectors. Therefore, in our simulations, only photon noise is generated for the CCD and photon noise plus multiplication noise is generated for the ICCD. Our simulations imply (Fig.5) that CCD detectors generally perform better than ICCD detectors owing mainly to the higher quantum efficiency of the photon detector. These results are confirmed experimentally.

II. Second year: 2006-2007

The following studies were undertaken:

1. Further development of the radiative model of LIP for both vacuum and atmospheric conditions. The model was used to calculate composition of materials based on spectral data, with no standards to use.
2. Application of the duplication curve method for self-absorption correction and improvement of analytical performance of LIP.

Calculation of radiation emitted by ellipsoidal asymmetric plasma into a finite size optical element (lens)

Our approach to standard-less analysis is based on comparison of spectra measured in experiment with those calculated via a theoretical model. The model, therefore, should adequately describe emission signal transformed through an experimental set-up. For a dynamic non-symmetric plasma (the one modeled in our approach), a solution of light collection and related radiative transfer problems presents certain difficulty. We solved this problem for the asymmetric ellipsoidal plasma (realistic in LIP) and light collection element (lens) placed in arbitrary position with respect to the plasma (Fig.6). Points on ellipsoidal plasma surface were

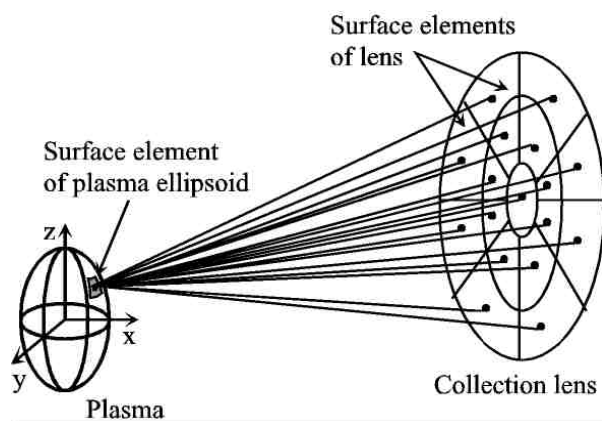


Figure 6. Radiation emitted by area element of plasma ellipsoid and collected by a collection lens

chosen for which radiation was calculated along a number of directions toward lens surface elements. Each such point was associated with an elementary surface area for which the radiation was assumed to be constant. The radiative transfer equation was solved along all corresponding directions inside the plasma and then total plasma emission was calculated collected by an optical element (lens). Errors associated with discretization schemes (concentric sectors on plasma and lens surfaces) and simplifying assumptions (flatness of the lens surface) were estimated and found to be insignificant.

Standardless spectral analysis using radiative model of LIP with Monte Carlo optimization

Our radiative model of LIP allowed back-calculation of the plasma composition. The model used experimentally obtainable data: LIP spectra, initial plasma size and initial plasma temperature. We performed calculations for plasmas expanding into vacuum and argon at atmospheric pressure. Calculations and measurements were performed on home-made copper standards doped with Si and Mg. Monte Carlo optimization was used for finding initial plasma temperature and number densities. Satisfactory agreement (within 10 %) was obtained between the computed and the experimental spectra. We were able, therefore, roughly evaluate the plasma composition and plasma temperature using easily measurable initial plasma size and plasma spectrum. If stoichiometric ablation is assumed, the method allows standard-less elemental analysis of solid samples. Our results clearly demonstrate that on the basis of the model, the inverse problem, e.g., the determination of intrinsic plasma characteristics from the experimentally determined parameters, can be solved.

Evaluation of optical thickness of LIP by duplication factor approach

Quantitative LIBS strongly relies on proportionality between the elemental concentration and the corresponding emission signal. For many emission lines, this proportionality is lacking due to strong self-absorption in the plasma plume. The traditional duplication curve method is proposed to rapidly evaluate the optical thickness of a laser induced plasma at multiple wavelengths and to select emission lines suitable for quantitative analysis. Duplication curves (DC) relate the duplication factor to the atomic density. DCs are obtained by doubling either the plasma absorption length or the analyte concentration. DCs are closely related to curves of growth being their derivatives. Measurements with a back mirror to double the absorption length (Fig.7) were carried out for cast iron standards in which concentrations of minor components (Mn, Si, Cu, Ni, Mo, V, etc.) varied between 0.01 and 10 %. The results (Fig.8) were verified by computer simulations.

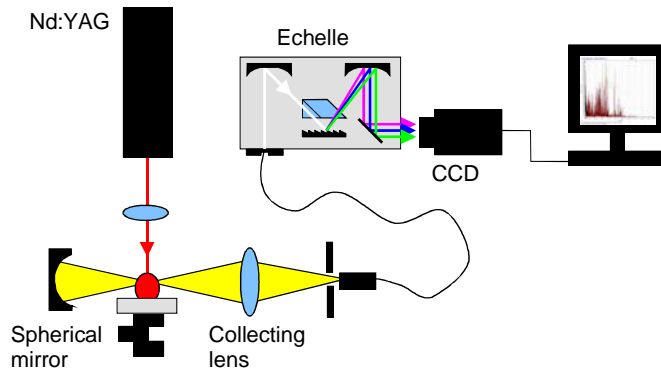


Figure 7. Experimental arrangement for measuring duplication factors.

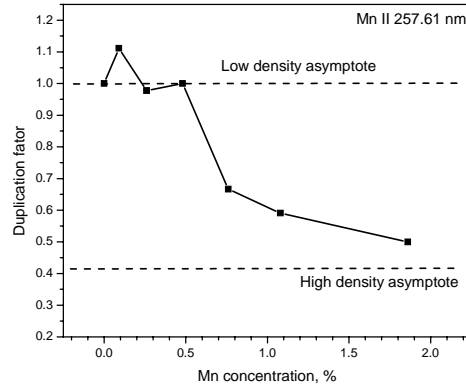


Figure 8. Example of DC for Mn II 257.61 nm line. Line is not self-absorbed or self-reversed at concentrations below 0.5 %.

We, thus, conclude that simulations and experiment show that the duplication curve method is well suited in laser-produced plasmas. The benefits are obvious: 1) only one or few measurements are necessary to verify or disprove line self-absorption; 2) experimental arrangement with a spherical back mirror is feasible; 3) additional plasma diagnostic is possible based on the shape of DCs or curves of growth (a-parameter, broadening mechanisms, etc.)

III. Third year: 2007-2008

The following theoretical and experimental works have been accomplished.

1. Further improvement of the model of LIP by solving the problem of collection of plasma radiation. An arbitrary optical system (a lens or fiber) placed in the arbitrary position with respect to the plasma was incorporated into the model.
2. Modeling radiative transfer for a plasma containing aerosol particle.
3. Experimental study of the radiation emitted by an asymmetric plasma.
4. New look at the correlation approach for material identification and plasma diagnostic; comparison of linear and rank correlations.

Radiation from asymmetric laser induced plasma collected by a lens or optic fiber

This work is the generalization of the approach proposed earlier for calculation of radiation emitted by ellipsoidal asymmetric plasma into a finite size optical element (see above). The essential part of this generalization is the ability of the theoretical model to calculate plasma radiation for arbitrary position and orientation of optical elements (lenses or fibers).

In brief, each infinitesimal surface element of the lens receives the amount of radiation which depends on the current orientation of the plasma ellipsoid. For each surface element, a unique set of straight line segments exists along which the radiative transfer equation is solved. A simple parameterization of all such sets is proposed and illustrated in Fig.9.

The optical fiber collects the incident radiation within only its acceptance cone. The fiber may or may not see the plasma during its expansion, or may see only its portion. An efficient algorithm is proposed also for this case.

experimentally observed differences in line intensities (Fig.10) are up to 40 %. Since the variances of the measurements conform to the error of the method the difference in limits of

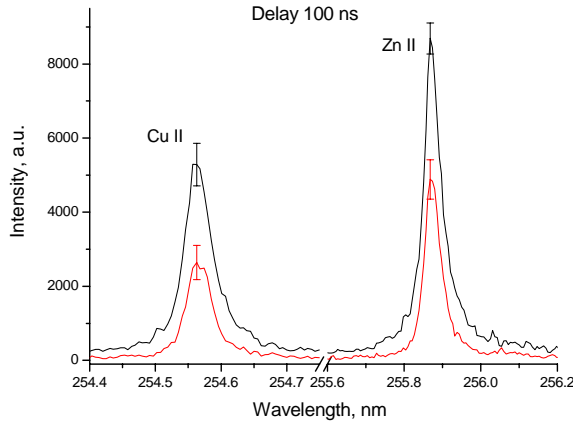


Figure 10. Spectra of an initial ellipsoidal plasma measured with a delay of 100 ns and a time window of 50 ns in vacuum. The spectra resulting from the detection along the long plasma axis show higher line intensities than the one along the short axis.

detection (LOD) would also amount 40 %. Consequently, different observation geometries affect the LOD. We, therefore, conclude that the plasma asymmetry affects the sensitivity of the method. For a reliable quantitative analysis, the plasma asymmetry has to be considered. Thus, the results of this study may have implications for spectrochemical analysis by LIBS and for plasma diagnostics.

Deeper look at linear and rank correlations used for material identification in LIBS. Discovering a potential of linear correlation analysis for plasma diagnostics

The purpose of this work is to critically assess the potential and limitations of linear and rank correlation methods, not only relevant to laser induced breakdown spectroscopy (LIBS) but to other spectroscopic techniques as well. Through computer simulations, it is demonstrated that

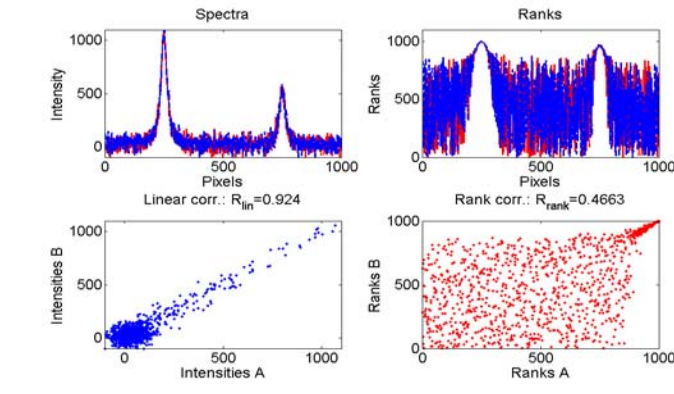


Figure 11. Linear (left) and rank (right) correlations of synthetic spectra with superimposed random noise.

a linear correlation is more suitable technique for material identification than a rank correlation due to its better stability toward noise and better ability to detect small systematic variations in line intensities (Fig.11). Effect of noise on results of correlation analysis has been studied. It is found that random noise causes correlation coefficients to be distributed normally, whereas flicker noise (random fluctuations in line intensities) results in a gamma distribution of correlation coefficients. Hence, the distribution of correlation coefficients can be used for detection of the type of noise that dominates correlated spectra.

A potential of linear correlation analysis for plasma diagnostics is demonstrated. It is based on the strong dependence of the linear correlation coefficient upon the shapes of correlated

spectral lines and, consequently, upon a state of the plasma (plasma temperature, number densities) which determines the line shapes. A linear correlation curve method similar to the curve of growth method is developed based on the dependence of the linear correlation coefficient upon the analyte concentration (Fig.12). The method can be used for determination of a plasma damping parameter and for a quick check of line self-absorption.

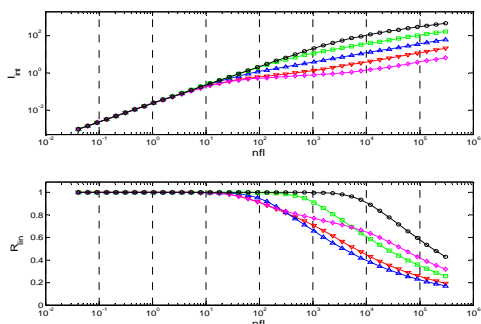


Figure 12. a) Theoretical curves of growth (COG) calculated from the plasma model [16] for Ba I 413.066 nm line; b) Linear correlation curves (LCC) calculated for the same line.

IV. Conclusions

The main result of our efforts is the development and successful application of the theoretical model of laser induced plasma (LIP) that allows a back-calculation of the composition of the plasma (and the condensed phase) based on the observable plasma spectrum. The model has an immediate experimental input in the form of LIP spectra and a few other experimentally determined parameters. The model is also sufficiently simple and, therefore, practical. It is conveniently interfaced in a graphical user-friendly form for using by students and any laboratory personnel with only minimal training. In our view, the model opens up the possibility for absolute analysis, i.e. the analysis which requires no standards and tedious calibration. The other parts of this proposal (including plasma diagnostics) were somewhat subordinate to this main goal. Plasma diagnostics provided the model with the necessary experimental input and led to better understanding of plasma processes.

Another fruitful direction we pursued was the use of the correlation analysis for material identification and plasma diagnostics. Through a number of computer simulations we achieved a clear understanding of how, where and why this approach works being applied to emission spectra from a laser plasma. This understanding will certainly improve the quality of forensic and industrial analyses where fast and reliable material identification and sorting are required.

Publications Acknowledging DOE Support – 2005-2008

1. I.B. Gornushkin, A.Ya. Kazakov, N. Omenetto, B.W. Smith, J.D. Winefordner, *Experimental verification of laser induced plasma expanding into vacuum*, Spectrochim. Acta Part B 60 (2005) 215-230.
2. A.Ya. Kazakov, I.B. Gornushkin, N. Omenetto, B.W. Smith, J.D. Winefordner, *Radiation dynamics of post-breakdown laser induced plasma expanding into ambient gas*, Appl. Optics 15 (2006) 2810-2820.
3. I.B. Gornushkin, S.V. Shabanov, N. Omenetto, J.D. Winefordner, *Non-isothermic asymmetric expansion of laser-induced plasma into vacuum*, J. Appl. Physics 100 (2006), 073304.
4. A.Ya. Kazakov, I.B. Gornushkin, N. Omenetto, B.W. Smith, J.D. Winefordner, *Two-temperature radiative model of laser induced plasma expanding into vacuum*, in preparation (2008).
5. M. Mueller, I. B. Gornushkin, S. Florek, D. Mory, and U. Panne, *Approach to Detection in Laser-Induced Breakdown Spectroscopy*, Anal. Chem. (2007) 4419 - 4426

6. U. Heitmann, I. B. Gornushkin, M. Mueller, N. Omenetto, J. D. Winefordner, U. Panne, *Evaluation of optical thickness of laser induced plasma by duplication factor approach*, in preparation (2008).
7. E. Tognoni, G. Cristoforetti, S. Legnaioli, V. Palleschi, A. Salvetti, M. Mueller, U. Panne, I. Gornushkin, *A numerical study of expected accuracy and precision in Calibration-Free Laser-Induced Breakdown Spectroscopy in the assumption of ideal analytical plasma*, Spectrochim. Acta Part B 62 (2007) 1287-1302
8. P.S. Dalyander, I.B. Gornushkin, D.W. Hahn, *Numerical simulation of laser-induced breakdown spectroscopy: Modeling of aerosol analysis with finite diffusion and vaporization effects*, Spectrochim. Acta Part B, In Press, 2008
9. S.V. Shabanov, I.B. Gornushkin, J.D. Winefordner, *Radiation from asymmetric laser-induced plasmas collected by a lens or optical fiber*, Appl. Optics, In Press, 2008.
10. I.B. Gornushkin, M. Mueller, U. Panne, J.D. Winefordner, *Linear and rank correlation for material identification in laser induced breakdown spectroscopy and other spectral techniques: a deeper look*, Appl. Spectrosc., In Press, 2008
11. E.M. Rodriguez, I.B. Gornushkin, J.R. Almirall, N. Omenetto, J.D. Winefordner, *Laser Induced Breakdown Spectroscopy as a tool for discrimination of glass for forensic applications*, in preparation (2008)
12. E.M. Rodriguez, I.B. Gornushkin, M. Tripathi, N. Omenetto, B. Smith, J.D. Winefordner, *Analysis and Identification of Solid Materials by Laser Induced Breakdown Spectroscopy: Comparative Study with Four Spectrometers*, in preparation (2008)

Presentations

1. N. Omenetto, I.B. Gornushkin, B.W. Smith, J.D. Winefordner, *Lasers at work in atomic and molecular spectrometry: recent developments and applications*, Colloquium Spectroscopicum Internationale XXXIV, Antwerp, Belgium, 4 - 9 September, 2005.
2. I.B. Gornushkin, *Radiative model of post-breakdown laser induced plasma*, Invited talk in the Federal Institute for Materials Research and Testing (BAM), October 21, 2005.
3. I.B. Gornushkin, S.V. Shabanov, N. Omenetto and J.D. Winefordner, *Radiative model of non-symmetric three dimensional expansion of laser induced plasma into vacuum*, Winter Plasma Conference 2006, Tucson, AZ, January 8-14, 2006.
4. I.B. Gornushkin, *Correlation analysis in laser induced breakdown spectroscopy*, Elemental Analysis of Forensic Evidence Workshop, Florida International University, Miami, FL, February 27- March 3, 2003.
5. J.D. Winefordner, B.W. Smith, N. Omenetto, I.B. Gornushkin, *Modeling and application of laser induced plasma*, DOE contractors meeting, Airlie Center, Warrenton, VA, April 23-26, 2006.
6. I.B. Gornushkin, S.V. Shabanov, N. Omenetto and J.D. Winefordner, *Non-isothermic asymmetric expansion of laser induced plasma into vacuum*, 4th International Conference LIBS 2006, September 2-9, 2006, Montreal, Canada.
7. I.B. Gornushkin, U. Heitmann, G. Moore, M. Mueller, B.W. Smith, N. Omenetto and J.D. Winefordner, *Evaluation of optical thickness of laser induced plasma by duplication factor approach*, FACSS, September 24-28, 2006, Lake Buena Vista, FL.
8. I.B. Gornushkin, S.V. Shabanov, N. Omenetto, J.D. Winefordner, *Radiation from an asymmetric laser induced plasma collected by a lens or optic fiber*, EMS LIBS 2007, September 10-13, 2007, Paris, France

Patents and Copyrights

1. I.B. Gornushkin, B.W. Smith, J.D. Winefordner, *"The method of reliable material identification"*, Patent, UF#-10947 (2006).